The Charge Reduction Rate for Multiply Charged Polymer Ions via Ion-Ion Recombination at Atmospheric Pressure

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Supporting Information

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Determination of the Limiting Sphere Radius

As noted in the main text, the limiting sphere radius needs to be sufficiently large to have no bearing on calculation results. Using Fuchs’s formula\(^1\) for the limiting sphere radius, we arrived at \(\delta_{Fuchs}=352.2\) Å for PEG\(_{4600}^{z^+}\) and NO\(_2\) collisions. In previously studying recombination of singly charged ions, we found that use of \(\delta_{Fuchs}\) as the limiting sphere radius was sufficient. However, as shown in Figure S1, \(\delta>\delta_{Fuchs}\) was required in the present study. We obtain similar results for the \(z=2−7\) ions, and hence utilize \(\delta=5.0\delta_{Fuchs}\) for these charge states, while for \(z=1\) we utilize \(\delta=3.0\delta_{Fuchs}\).

**Figure S1.** The recombination rate for (a) \(z=7\) and (b) \(z=1\) PEG\(_{4600}^{z^+}\) ions as a function of the limiting sphere radius utilized in simulations.
Partial charges of atoms in $\text{PEG}_{4600}^{z^+}$ and $\text{NO}_2^-$

**Table S1.** Partial charges on atoms used in MD simulations.

<table>
<thead>
<tr>
<th>Molecular type</th>
<th>Atom</th>
<th>Charge [\text{-}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG (At chain end)</td>
<td>H on O</td>
<td>0.435</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-0.7</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.145</td>
</tr>
<tr>
<td></td>
<td>H on C</td>
<td>0.06</td>
</tr>
<tr>
<td>PEG (At middle of chain)</td>
<td>O</td>
<td>-0.4</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>H on C</td>
<td>0.03</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>N</td>
<td>-0.8</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.45</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>N</td>
<td>0.046</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-0.523</td>
</tr>
</tbody>
</table>
Ion induced dipole potential

The ion-induced dipole potential \( U_{\text{ind}} \) between a unit charge and the center of an induced dipole is given by the equation:

\[
U_{\text{ind}} = -\frac{ae^2}{8\pi\varepsilon_0 r^4}
\]  

(S1)

where \( \alpha \) is background gas molecule’s polarizability (1.7 Å\(^3\) for N\(_2\)), \( r \) is the distance between the gas molecule center and the charge, and the other parameters are defined in the main text. To implement this potential in MD simulations, the ion-gas molecule distance \( r \) was calculated from N\(_2\) gas molecule and NH\(_4^+\) (or NO\(_2^-\)) ion centers of mass \( (r=r_{\text{gas}}-r_{\text{ion,center}}) \). Then, the calculated potential, \( U_{\text{ind}} \), was directly added to potential working on the N\(_2\) molecule, while the product of the potential and mass ratio, \( U_{\text{ind}} \frac{m_{\text{atom}}}{m_{\text{ion}}} \), was imparted to each atom within NH\(_4^+\) and NO\(_2^-\) ions. While partial charges were applied to all atoms in PEG\(_{4600}^{z^+}\), partial charges where not considered in induced dipole calculations.
Measurement of the ion concentration generated from radioactive source

Ion concentration measurements in the mixing chamber were approximated using the experimental setup depicted in Figure S2. The experimental setup is similar to that depicted in Figure 2b, but with the electrospray ion source removed. At variable bipolar ion source flow rates \( Q_{\text{Am}} \) with constant total system flow rates, the concentration of ions upstream and downstream of the mixing chamber, \( N_{\text{ion,in}} \) and \( N_{\text{ion,out}} \), respectively were measured by an ion counter, similar in design to the ion trap described by Adachi et al.\(^2\) Unsurprisingly, we observed that the concentration of ions decreased through the chamber due to deposition of ions on the chamber walls. Therefore, in comparing measurements to models, we utilized the logarithmic average of two ion concentrations \( (N_{\text{ion,in}} \) and \( N_{\text{ion,out}} \)), with the formula used provided in Figure S2. The resulting mean ion concentrations, along with the inlet and outlet ion concentrations, are shown in lower left panel of Figure S2. The ion concentration increased with increasing flow rate through the \(^{241}\text{Am} \) chamber, \( Q_{\text{Am}} \).

**Figure S2.** A schematic diagram of the experimental setup used in measurement of mean ion concentration in the mixing chamber. Measurement results are provided in the lower left.
Initial charge distribution of electrosprayed PEG\textsubscript{4600}\textsuperscript{z+} ions

The mass-to-charge ratio distribution of PEG\textsubscript{4600}\textsuperscript{z+} as electrosprayed is shown Figure S3. To obtain an initial charge distribution from this spectrum, we first estimated the mass distribution of the PEG\textsubscript{4600} sample by fitting to the electrical mobility distribution of singly charged PEG ions. Fitting to this distribution is shown in Figure S4. Electrical mobility (\(Z_p\)) was converted to mass (\(M_w\)) using relationship, \(Z_p^{-0.5} = 0.0936M_w^{1/3} + 0.355\), established by Saucy et al.\textsuperscript{3} Through fitting a mean \(<M_w> = 4,339\) Da and standard deviation of \(\sigma = 413\) Da was obtained for the mass distribution. Second, using this mass distribution, we fit the mass-to-charge ratio distribution by a least squares method to determine the relative weightings of the distributions for different charge states (each distribution with mean \(<M_w>/z\) and standard deviation \(\sigma/z\)). This resulted in an initial charge distribution with 0.421 at \(z = 7\), 0.437 at \(z = 6\), 0.069 at \(z = 5\), 0.050 at \(z = 4\) and 0.023 at \(z = 3\).

![Graph showing mass-to-charge ratio distribution for PEG\textsubscript{4600}\textsuperscript{z+} as electrosprayed. The fit distributions for different charge states are also depicted, with the \(z = 7\) distribution occupying the lowest mass-to-charge ratio range.]

\textbf{Figure S3.} Mass-to-charge ratio distribution for PEG\textsubscript{4600}\textsuperscript{z+} as electrosprayed. The fit distributions for different charge states are also depicted, with the \(z = 7\) distribution occupying the lowest mass-to-charge ratio range.
Figure S4. A Gaussian fit of the singly charged PEG ion electrical mobility distribution, measured at $Q_{Am}/Q_{ES}=11$. Open circles are measurements, and black and red lines are fit lines for the singly charged monomer and aggregates, respectively.

References